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Abstract

# STUDY OF THE HIGH TEMPERATURE BEHAVIOUR OF URANIUM OXIDES AND OF THE KINETICS AND MECHANISM OF FORMATION OF URANIA-THORIA SOLID SOLUTIONS

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**The paper summarises the results of studies on the high temperature chemistry of the oxides in the system $UO_2$-$ThO_2$-$O_2$ with special reference to the kinetics and mechanism of formation of solid solutions. It is shown that the mechanism by which $U_3O_8$ reacts with $ThO_2$ in air at temperatures $\geqslant 1000^{\circ}C$ to form a solid solution involves a gas phase. The importance of this gas phase reaction in fabricating high density fuels is discussed. On the basis of a study of similar reactions with other oxides ($Al_2O_3$, $SiO_2$, CaO, $HfO_2$, $ZrO_2$ and stabilized $ZrO_2$), it is shown that the reaction involving gaseous $UO_3$ proceeds only if the substrate material on which it condenses has a cubic symmetry. Thus, no reaction is observed with non-cubic oxides [$Al_2O_3$, $SiO_2$, $ZrO_2$( below about $1250^{\circ}C$)], noticeable reactions with the high temperature pseudo-cubic modifications, and strong reactions with cubic oxides.**

For elucidating the kinetics of $U_3O_8$-$ThO_2$ reactions, the high temperature behaviour and kinetics of weight loss from nuclear pure $U_3O_8$ have been studied in the temperature range 1200-1500°C. The isothermal weight loss from $U_3O_8$ heated in air is found to vary linearly with exposed surface area and to follow a first order kinetics with an energy of activation of 104 kcal/mole and an entropy of activation of 30.5 e.u. In $U_3O_8$-$ThO_2$ mixtures there is a very sudden initial weight loss. The period over which this weight loss occurs increases with decreasing temperature. The end of this period corresponds with about 80% solid solution formation, after which the isothermal weight loss obeys first order kinetics with an energy of activation of 74 kcal/mole and an entropy of activation of 16.5 e.u. (values for 50 mole % mixture). The volatilizing species is a pure uranium oxide. This volatility of urania-thoria is discussed from the point of view of stability of such fuels at high temperatures.

The kinetics of solid solution formation obeys Jander's equation. Arrhenius plot gives an energy and entropy of activation of 41.5 kcal/mole and 6.3 e.u. respectively.

During the high temperature studies of $U_3O_8$ it is observed that on extremely slow cooling (100°/day) from temperatures greater than 1100°, a different phase of $U_3O_8$ appears. The structural relationship of this phase with the Rundle phase, and $\alpha$-$U_3O_8$ are discussed in terms of the "out-of-step" stacking faults.